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THERMOMETRY FIXED POINTS BASED ON BINARY EUTECTIC ALLOYS

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ABSTRACT

In this work investigations on binary eutectic alloys of gallium with aluminum, with zinc and with tin are presented. It was found that the gallium tin system with a phase-transition temperature of (20,477±0,004) °C is the most suitable fixed point. The definition of the phase transition temperature was based on the maximum of a histogram that shows percentage of time spent in consecutive temperature intervals for equilibrium melting curves. The results show that non-equilibrium effects are the most important influencing quantities. This requires slow freezing of these alloys to minimize the range and slope of the subsequent melting curves.

Index Terms – thermometry fixed-points, binary eutectic alloys, gallium-tin

1. INTRODUCTION

The definition of the International Temperature Scale of 1990 (ITS-90) is based on well-defined thermodynamic states of ideally pure substances [1]. At temperatures above -40 °C these are the triple point of water and freezing, melting or triple points of very pure metals. For the temperatures between these fixed points, standard platinum resistance thermometers (SPRTs) are defined as interpolation instruments. Because the characteristics of SPRTs is well understood, a small number of calibration points (fixed points) is sufficient. But, for most applications other types of thermometers have to be used. This is because of different reasons such as price, robustness or requirements regarding the size respectively geometry.

For these thermometers often alternative calibration methods and additional calibration points (temperatures) are needed. In many cases the so called comparison method is used. Here the calibration of the "industrial thermometer" is carried out in a "bath" with appropriate temperature stability and homogeneity by direct comparison with a calibrated SPRT. The disadvantage of this methodology is a larger measurement uncertainty compared to fixed-point calibrations.

A promising approach to overcome some difficulties is the use of so called secondary reference points (fixed-point), which are a matter of several research activities [2, 3]. These are based on the use of binary eutectic metal alloys. The developments have two aims, first to find a fixed point substance with a suitable transition temperature with excellent reproducibility and second to allow miniaturization in order to carry out in situ calibrations by means of so called miniaturized fixed-point cells. The latter ones are often designated as self-validating thermometers because the repeatability of the fixed-point realization is used to check and to correct the drift of the thermometer by an in situ calibration at regular time intervals [4, 5]. For several years both, self-validating thermometers and secondary reference-point cells are in use and partly commercially available. But so far these were developed for applications at higher temperatures and target uncertainties in the range between 50 mK and 200 mK. The main limitations at high temperatures are thermal imperfections of the furnaces or other thermal environments which limit further improvements.

Only few investigations were so far published for low temperature binary systems where thermal environments with excellent temperature homogeneity and stability on the millikelvin level are available [2, 3]. The outcome of investigations on binary gallium alloys is contradictory and results in uncertainty claims between 1 mK and 20 mK. For small-sized self-validating thermometers the strong supercooling of pure gallium and its alloys is a further challenge.

The paper is structured as follows. First we start with a summary of different approaches for the definition of the fixed-point temperature. Then we discuss physical processes which influence the reproducibility of the fixed-point realization. In the last part we present experimental results for binary alloys of gallium with zinc and tin to identify and quantify the significant sources of uncertainty.

2. DEFINITION AND DETERMINATION OF THE FIXED-POINT TEMPERATURE

For metal fixed points ITS-90 defines the liquidus temperature of the ideally pure substance as fixed-point temperature. In the following we skip the discussion about the methodology to quantify and correct the influence of remaining impurities on the phase transition temperature. We focus on the definition and comparison of methods for the determination of the fixed-point temperature of cells filled with very pure metals or binary eutectic alloys.

Although freezing or melting curves of very pure metals (6N to 7N purities) are very flat the segregation of remaining impurities and thermal effects require an agreement which part of such curves should be used for the determination, respectively approximation of the fixed-point temperature. The definition based on the liquidus temperature requires the measurement of the onset of freezing or end of melting. In both cases a measurement with an infinitesimal small amount of solid material is not feasible. Therefore, suitable procedures are needed to minimize and to quantify the influence of the impurity segregation during the measurement.

If the supercooling of a metal in a fixed-point cell is small the best approximation for the liquidus temperature is the maximum of the freezing curve. This is the recommended procedure for most metal fixed points [6].

Because gallium is known for its large supercooling its liquidus temperature is usually determined by means of melting curves. Due to the high purity of gallium the slope of a melting curve and the resulting uncertainty are very small.

If a binary eutectic alloy is considered, there is so far no generally accepted definition which point of a freezing or melting curve should be used as fixed-point temperature. In most cases melting curves are preferred [7, 8]. In the past fixed-point temperatures determined by means of melting curves were defined in a very different manner such as the onset of melting, the point of inflection, the run-off point, the melt-off point, the maximum or the centroid of a histogram that shows percentage of time spent in consecutive temperature intervals, or an extrapolated liquidus point.

The smallest melting range is usually achieved when a homogeneous liquid specimen has a eutectic composition and is frozen very slowly [7]. As a result most of the solid is in an equilibrium state with eutectic composition except for the excess primary phases formed immediately after nucleation and at the very end of the freezing process. Therefore, for the subsequent melting curve a definition of the phase transition temperature via the maximum of a histogram that shows percentage of time spent in consecutive temperature intervals (Fig. 1) seems to be the most appropriate approach.

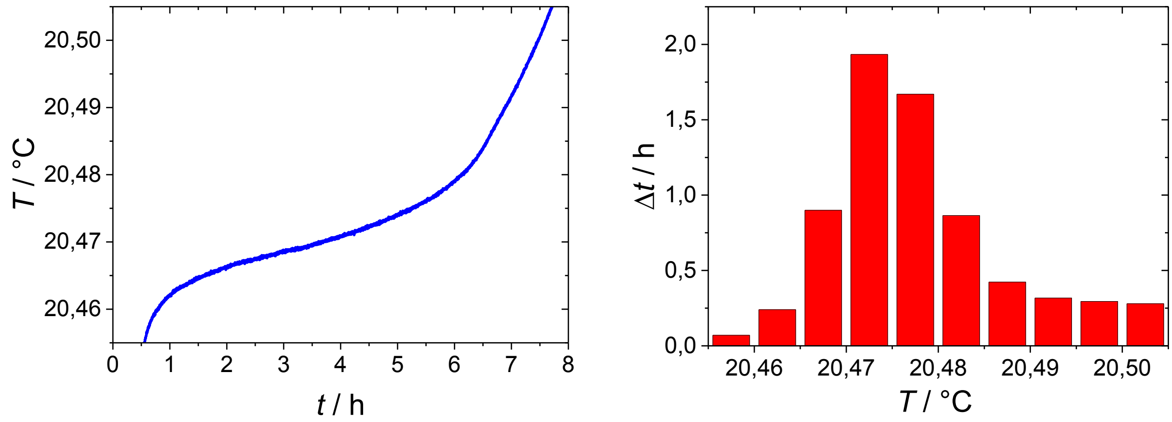

Figure 1 Example for a melting curve of a Ga-Sn eutectic and the corresponding histogram

3. INFLUENCING QUANTITIES

The quantities influencing the reproducibility of thermometry fixed points can be distinguished on the basis of three main causes for deviations. These are imperfections in the thermal design of fixed-point cell, thermometer and thermostat, fixed-point material related contributions and variations due to the method of the fixed-point realization.

The most important requirement for the geometric design of a fixed-point cell is the minimization of axial and radial heat losses via the thermometer and internal heat bridges. Important design parameters are the difference between fixed-point temperature and the temperature of the surrounding and restrictions due to the crucible material. Crucibles for gallium fixed-point cells are usually made of polytetrafluoroethylene, have an outer diameter of about 40 mm and a length of about 300 mm. The plateau durations of commercial cells are between 12 hours and several days and remain within ±50 µK. The inner diameter of the re-entrant well is typically about 8 mm to allow the calibration of SPRTs of different type. A miniaturization without degrading the measurement uncertainty is possible by matching the diameters of re-entrant well and SPRT and ensuring a specific minimum ratio between immersion length and SPRT diameter.

The curvature of freezing or melting curves of well designed fixed-point cells, operated in a suitable thermostat, is dominated by the amount and distribution of remaining impurities.

For the metal fixed points of the ITS-90 the melting behavior is considerably more sensitive to impurities than is the freeze. But for metals with large supercooling and eutectic fixed points the reproducibility of melting curves is always better than for freezing curves.

To achieve smallest possible uncertainties with melting curves of pure metals, the consideration of two influencing quantities is required. The first one is to avoid a segregation of the remaining impurities. This can be achieved by a very fast freezing procedure. The other disadvantage of melting curves is the increase of thermal effects with increasing liquid fraction. A solution of this problem requires the investigation and separation of thermal effects from changes of the plateau caused by impurity segregation. If these effects can be separated, an extrapolation of the melting curve towards the liquidus point is possible.

For binary alloys the situation is different because the dominating sources of uncertainty are based on non-equilibrium effects [7]. As a consequence the melting range is always considerably larger in comparison to pure metals. Figures 2 shows a typical melting curve of a slim gallium cell (details see next section), whereas in figure 3 for a cell with identical dimensions the melting curve of a eutectic Ga-Sn is presented.

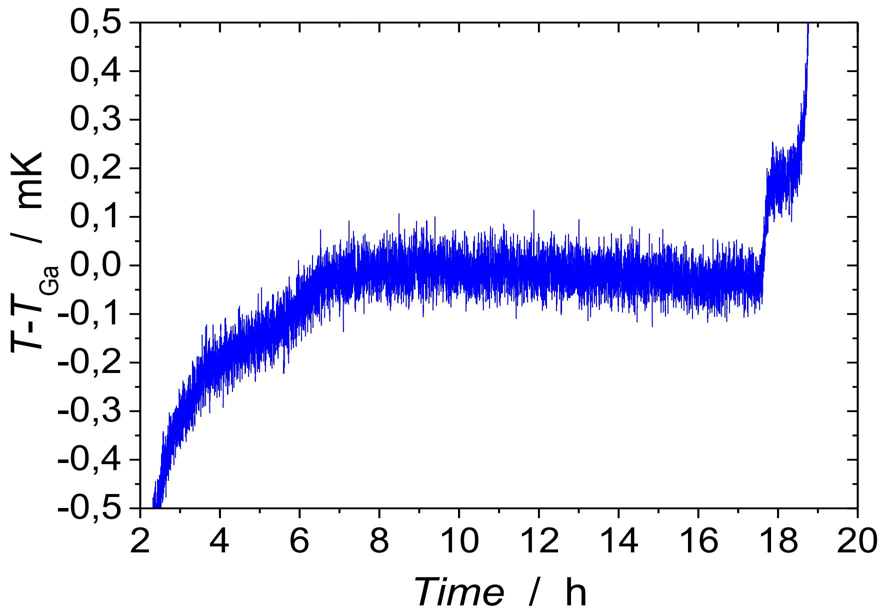

Figure 2 Melting curve of a slim gallium fixed-point cell

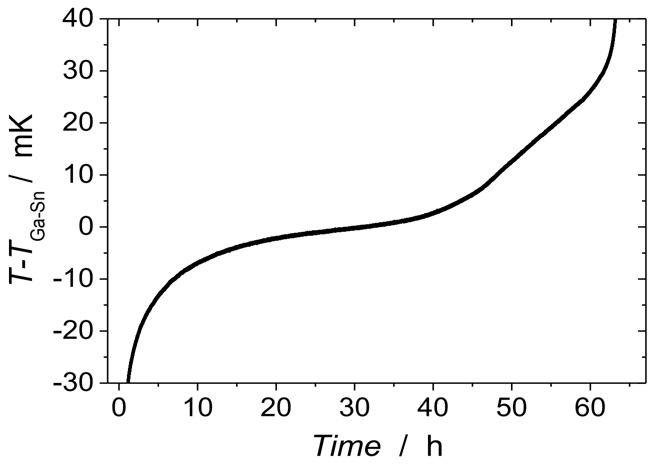

Figure 3 Melting curve of a slim fixed-point cell with a eutectic alloy of gallium with tin

The two main causes for non-equilibrium effects in metal binary eutectics are curved interfaces (Gibbs-Thomson effect) and composition variations [7]. Therefore, in contrast to pure metals a fixed point cell based on a eutectic should be always frozen very slowly to minimize the influence of non-equilibrium effects.

4. EXPERIMENTAL

The fixed-point cells were designed as slim-type for operation in a FLUKE type 9170 dry block calibrator. The crucibles were made of polytetrafluoroethylene, had an outer diameter of 25 mm and a length of 170 mm. After fabrication the cells were cleaned with nitric acid and afterwards purged and steam cleaned with ultrapure water. The cells were filled with gallium (1 cell) and eutectic mixtures of gallium with tin (4 cells), gallium with zinc (2 cells) and gallium with aluminium (2 cells). For the investigations gallium, tin and zinc with 7N purity and aluminium with 6N purity were used. The claimed purities are based on results of glow discharge mass spectrometry (typically 70 elements) provided by the manufacturers of the materials. These claims were confirmed by fixed-point measurements on ITS-90 cells manufactured at PTB from the same batches of material. To achieve sufficient mixing, the fixed-points were subjected to about 25 freeze/melt cycles, each followed by isothermal phases larger than one hour in the liquid state.

The measurements were carried out by means of a metal-sheated SPRT and an ISOTECH micoK-70 measurement system at a current of 1 mA. A calibration of the SPRT was carried out at the triple point of water and the gallium point at PTB. The resulting uncertainty of the temperature measurement is smaller than 1 mK including self heating (<0,3 mK) and pressure related effects (i.e. atmospheric pressure and hydrostatic head).

5. RESULTS AND CONCLUSIONS

The measurements on the Ga-Al system showed an insufficient reproducibility and a considerable rounding of the melting plateaux. The resulting fixed-point temperature was about 26,92 °C with a reproducibility of about 50 mK. Therefore, this system was excluded from further investigations.

In a next series of measurements the eutectic alloy of gallium with zinc was studied. First the freezing was carried out by fast (-20 K/min) cooling and freezing of the liquid alloy at 10 °C, in order to study the influence of non-equilibrium effects. The results (Fig. 4) show that the slopes of the subsequent melting curves and the melting range of this alloy indicate a non-equilibrium state. By using a very slow melting rate it is possible to shift this alloy towards an equilibrium state but this is very time consuming and requires plateau durations larger than 50 hours. Ancsin [8] described similar findings for his adiabatic experiments on eutectic Al-Cu and Al-Ag samples.

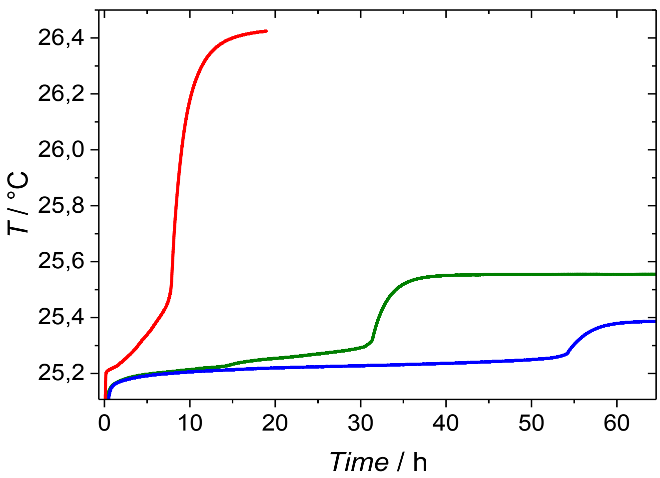

Figure 4 Melting curve variation of a Ga-Zn cell after non-equilibrium freezing, for different temperatures of the thermostat (25,4 °C, 25,55 °C and 26,45 °C)

For the eutectic Ga-Zn system a fixed-point temperature of (25,21 ± 0,03) °C was determined. Experiments showed that the reproducibility of the phase transition temperature of the eutectic Ga-Sn alloy in considerably better than for Ga-Zn. Therefore, further experiments were carried out on the eutectic Ga-Sn system. If the freezing was realized at almost equilibrium conditions (22 h duration) the subsequent melting range variation with heating rate was considerably smaller than for the Ga-Zn system (Fig. 5).

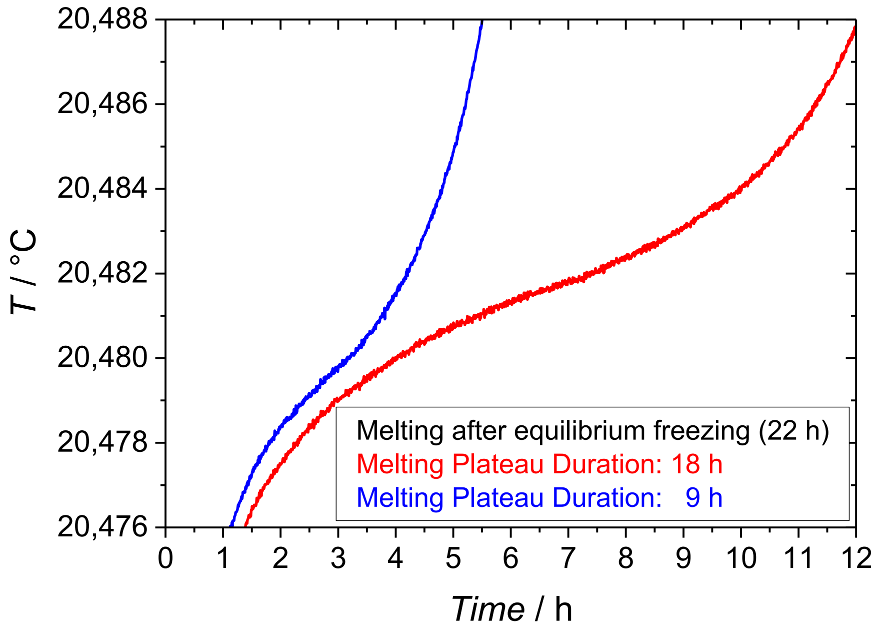

Figure 5 Melting curve variation of a slim fixed-point cell with a eutectic alloy of gallium with tin after equilibrium freezing

This was confirmed by the much smaller variation of the melting curve as a function of the preceding freezing rate (Fig. 6)

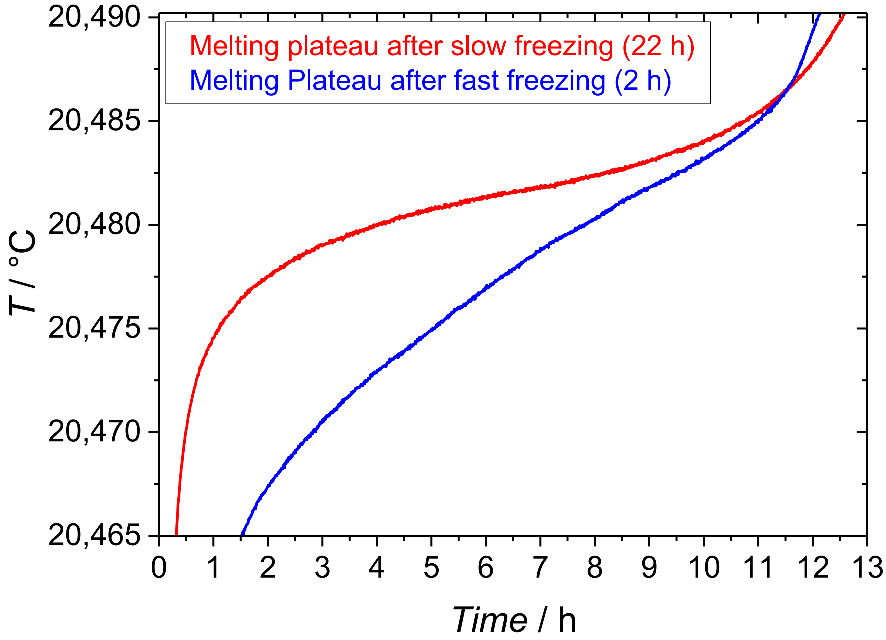

Figure 6 Melting curve of a slim fixed-point cell with a eutectic alloy of gallium with tin at different freezing rates

The long-term reproducibility of the Ga-Sn eutectic was investigated for 3 cells during a period of 18 months and compared with the result of a new cell (Fig. 7).

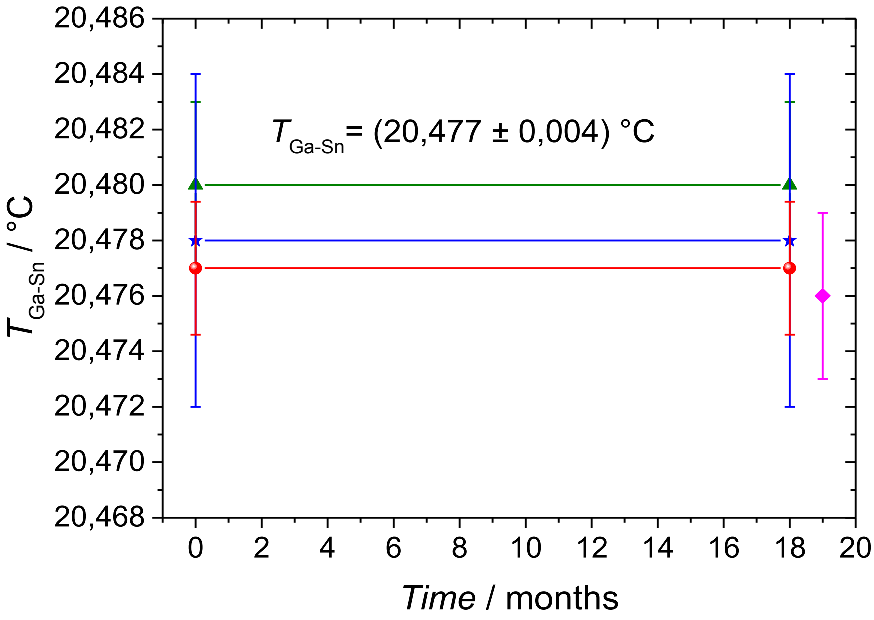

Figure 7 Reproducibility and long-term stability of the fixed-point temperature of a Ga-Sn eutectic alloy for 3 cells, the new cell is denoted with a diamond

Summarizing, in this work the definition of the phase transition temperature was based on the maximum of a histogram that shows the percentage of time spent in consecutive temperature intervals for equilibrium melting curves.
The results show that thermometry fixed points based on a eutectic Ga-Sn alloy are superior to eutectic Ga-Al and Ga-Zn systems and have a fixed-point temperature of (20,477 ± 0,004) °C. This result is in agreement with former findings [2, 3]. It was found that non-equilibrium effects are the most important influencing quantities. This requires slow freezing of these alloys to minimize the range and slope of the subsequent melting curve.

6. ACKNOWLEDGEMENTS

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